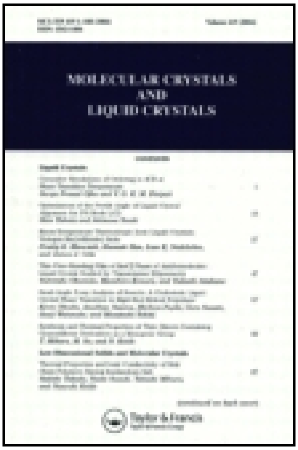

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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The Twisted Nematic Effect: Liquid Crystal Displays and Liquid Crystal Materials

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The Twisted Nematic Effect: Liquid Crystal Displays and Liquid Crystal Materials

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The rapid progress of the young liquid crystal display (LCD) technology is due to the synergisms resulting from combining research on electro-optical effects, liquid crystal materials and display technology. The design and production of liquid crystal molecules with specific physical properties and their application in displays based on the twisted nematic effect has led within only seventeen years from simple digital watch displays to high information content LCDs capable of reproducing color television pictures or graphics information on flat computer terminals. After reviewing those liquid crystal material parameters which strongly affect the display performance, the operating principle of the twisted nematic effect and its dependence on liquid crystal material properties is described.

The elastic, dielectric viscous, optical and mesomorphic properties of liquid crystals depend on specific molecular structural elements, such as on different hydrocarbon side chains, rigid cores and polar end groups. By specifically designing the molecules, synergetic effects are shown to result allowing to optimize the display performance and opening up new LCD applications.

The strong demand for large area, direct view and projection LCDs capable of reproducing high information contents not only requires new liquid crystals and actively addressed display substrates but often also new electro-optical effects with steep transmission-voltage characteristics such as those resulting from supertwisted nematic configurations. The black-white optical mode interference effect is shown to be one possibility to achieve—in combination with appropriate LC-materials—the required steep characteristics of highly multiplexed future LCDs.

1. INTRODUCTION

The first observation of liquid crystalline phenomena in organic compounds dates back to the last century. In 1888 the Austrian botanist Reinitzer attributed the optical anisotropies which he observed in molten cholesteryl benzoate under the polarizing microscope to a liquid crystalline mesophase. The term mesophase was introduced to characterize the liquid crystalline phase as being intermediate between the solid crystalline and the ordinary isotropic phase. Although mesomorphism over narrow temperature ranges is not uncommon among organic compounds, the scientific community, except for a few specialists, paid little attention to liquid crystals during the eighty years following the observations of Reinitzer. Therefore, until the late 1960s, only a few compounds—most of them exhibiting negative dielectric anisotropy—such as MBBA[1] (methoxy benzilidene butyl aniline) and PAA[2] (para azoxy anisole)—were used within their respective limited mesophases as standard materials for experimental purposes. The prerequisites and the motivation for designing liquid crystals with specific physical properties hardly existed. Liquid crystals were unknown to the man in the street.

The remarkable development of the liquid crystal field since the early 1970s and the subsequent extended use of liquid crystals in consumer and professional products, is closely connected with (i) the discovery of applicable electro-optical field effects, (ii) the design and production of liquid crystal materials with specific physical properties, and (iii) the development of display manufacturing processes making use of (i) and (ii). This development had its roots in the late 1960s when industrial research groups in the United States and Europe became interested in the strongly anisotropic and dielectric properties of liquid crystals. Attempts were made to affect the appearance of thin liquid crystal layers by external electric fields. The aims were to understand better the fascinating liquid crystalline properties. This knowledge was then used in the search for electro-optical effects for the realization of electrically tunable, flat, optical shutters. In 1968 Heilmeier and Zanoni[3] at RCA, Princeton, discovered that light scattering occurs in thin layers of negative dielectric anisotropic liquid crystals upon passing an ion current through the layers. This dynamic scattering (DS)-effect was the basis for the first liquid crystal displays in electronic wrist watches. However, besides the competition from the rapidly developing and established solid state display devices, such as light emitting diodes and vacuum fluorescent displays, the DS-effect had a number of basic drawbacks, such as rather large voltage and power requirements, poor viewing properties as well as a sluggish appearance of the optical signal versus applied voltage.

In 1971 Schadt and Helfrich[4] in Basel, Switzerland, and later Fergason[5] in Kent, United States, filed patents on an electro-optical field effect which has become known as the Twisted Nematic (TN)-effect. Its principle will be described below. Since no ionic current is required to generate an optical signal with the twisted nematic configuration, displays based on the TN-effect exhibit an extremely low power consumption of a few microwatts per square centimeter. This aspect as well as several other favourable properties have—in principle—made the twisted nematic effect an interesting candidate for display applications. However, in the early 1970s no liquid crystals were available with suitable physical properties which would for instance have allowed to operate twisted nematic liquid crystal displays (TN-LCDs) reliably at room temperature. Besides, TN-LCDs require two polarizers as well as surface alignment of the liquid crystal molecules at the display boundaries. Thus, their principle is rather elaborate and cumbersome compared with DS-LCDs and it was uncertain whether the surface aligning interactions would survive extensive lifetime tests and whether the 50% light absorption by the polarizers would be acceptable. Moreover, most solid state physicists were rather skeptical about the use of any operational organic materials in electronic devices, including the at the time exotic liquid crystals. Therefore, it was not at all obvious in the early 1970s that TN-LCDs would initiate a rapidly growing new display technology. Neither was it obvious that the Japanese watch and electronics industry would take the risks, enter the field and intensively develop the necessary manufacturing processes to realize TN-LCDs on an industrial scale. Moreover, it was not obvious that the sophisticated new field of liquid crystal material research which we know today would develop and promote many new LCD applications.

In the following some aspects of the development and the potential of these young technologies with their considerable commercial and social impact will be presented. A potential which was first verified in digital twisted nematic watch and calculator displays and which now allows to realize flat, high information content colour displays for computer terminals, television screens and large area information boards. This rapid progress is a result of the inspiring interdisciplinary and international collaboration between physicists, organic chemists, electronics- and display engineers.

Correlations between the electro-optical performance of the up to now almost exclusively used twisted nematic LCDs, highly twisted nematic LCDs and liquid crystal material properties will be presented. They illustrate how electro-optical effects in conjunction with molecular design techniques and measuring methods for determining the relevant liquid crystal material parameters developed in the recent history of liquid crystals, thus establishing and further improving the potential of the LCD technology.

2. SOME LIQUID CRYSTALLINE PROPERTIES

The unique anisotropic optical, electrical, magnetic and mechanical material properties of liquid crystals (LCs) are fundamental for their applicability in liquid crystal displays (LCDs). They result from molecular-specific electronic and steric anisotropies, combined with anisotropies resulting from long-range intermolecular interactions.[6] The long-range interactions, which are characteristic of mesophases, cause the long axes of the rod-shaped liquid crystal molecules to align preferentially parallel over macroscopic distances. This leads to symmetries of the arrangement of LC-molecules which are similar to those in solid crystals. The temperature dependent preferred direction of alignment is defined by the nematic director $\hat{n}$ (Figure 1). Figure 1 shows a typical phase sequence of a nematic liquid crystal.

Since the material properties of liquid crystals are the result of their molecular properties amplified by the long-range intermolecular order of the liquid crystalline state, the proper design of liquid crystal molecules for each specific electro-optical effect and its many applications is crucial. The top of Figure 2 shows the general construction principle of a rod-shaped liquid crystal molecule which consists of the dashed rigid core comprising aromatic or non-aromatic ring sys-

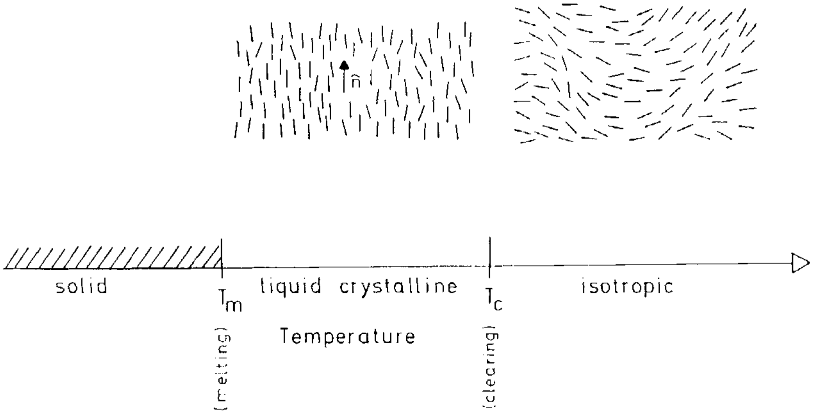


FIGURE 1 Solid-nematic-isotropic phase sequence. The nematic director $\hat{n}$ defines the preferred direction of the long molecular axes in the nematic phase. The degree of order S of the long molecular axes in the nematic phase is given by $S = 1/2 < 3 \cos^2 \theta - 1 >$, where θ = angle between $\hat{n}$ and the long molecular axis. T_m = melting temperature, T_c = transition temperature of the nematic-isotropic first-order phase transition (clearing temperature). The nematic long-range order abruptly disappears at T_c, causing $S(T \geq T_c) = 0$.

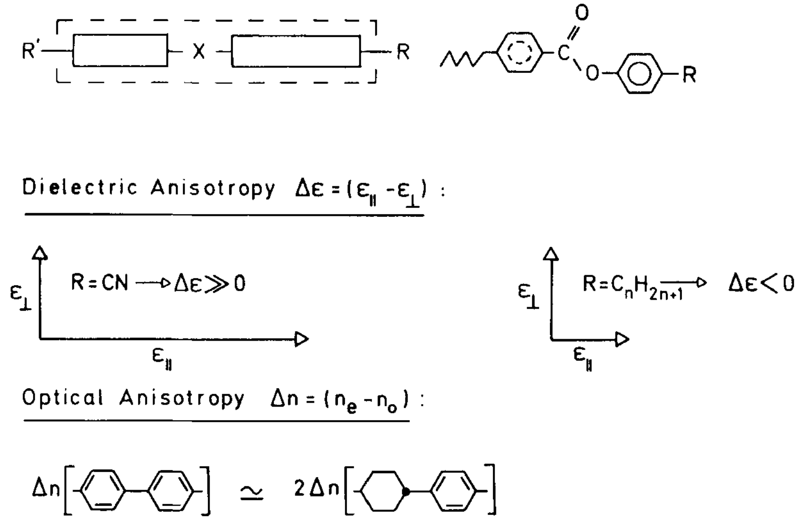


FIGURE 2 Top: Construction principle of a liquid crystal molecule with substituent *R*, the (dashed) rigid core and a flexible side chain *R'*. Middle: The dielectric anisotropy $\Delta\epsilon = (\epsilon_{\parallel} - \epsilon_{\perp})$ is strongly affected by the substituent *R*. R = CN leads to a positive dielectric anisotropic compound with $\Delta\epsilon > 0$. Bottom: The optical anisotropy $\Delta n = (n_e - n_o)$ is mainly determined by the aromatic rings and the degree of conjugation in the rigid core.

tems to which the rests R, R' are attached; where R' is in general a hydrocarbon side chain. The ester on the upper right of Figure 2 is a practical example. If a strong permanent dipole moment pointing along the long molecular axis is required, the cyano group $-C \cong N$ is often used. For R = CN a strong positive dielectric anisotropy $\Delta\epsilon = (\epsilon_{\parallel} - \epsilon_{\perp}) >> 0$ results,[7] where $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are the respective dielectric constants parallel and perpendicular to the nematic director. On the other hand, the replacement of R by a second hydrocarbon side-chain strongly reduces $\epsilon_{\parallel}$ and causes—because of the now predominant lateral ester moment—the dielectric anisotropy to change sign, that is, $\Delta\epsilon < 0$.[8] Thus, by properly selecting R and R' the dielectric anisotropy can be affected such that the molecules align either parallel to an applied electric field (for $\Delta\epsilon > 0$) or perpendicular to it (for $\Delta\epsilon < 0$).

Since the refractive indices of organic compounds depend on the degree of conjugation of π-electrons along a given molecular direction, the sterically and electronically anisotropic and ordered liquid crystal molecules give rise to an optical anisotropy $\Delta n = (n_e - n_o)$, with the respective extraordinary and ordinary refractive indices n_e

and n_o. Schematically this is illustrated at the bottom of Figure 2 where the biphenyl core on the left leads to an about twice as large optical anisotropy as the phenylcyclohexane core on the right with its non-aromatic cyclohexane ring.

The extent to which the dielectric anisotropy of liquid crystals can be affected by incorporating polar groups at different positions in a molecule is shown by the pyrimidines[9] in Figure 3. The large overall longitudinal dipole moment which follows from the superposition of the moments of the pyrimidine nitrogens with that of the cyano end group in type XP_1P pyrimidines leads to the large dielectric anisotropy $\Delta\epsilon > 20$ at $T << T_c$ (Figure 3). Shifting the pyrimidine nitrogens into position 2 and exchanging the benzene ring P by P_2 leads to the nematic pyrimidines of type XPP_2 on the left of Figure 3. In this case the pyrimidine nitrogen dipole moments diminish $\epsilon_{\|}$ and strongly reduce the dielectric anisotropy to $\Delta\epsilon \sim 4$.

Besides their optical and dielectric anisotropies, liquid crystals also exhibit anisotropic flow behavior which determines their dynamics. The flow anisotropies can be characterized by five different viscosity coefficients.[10] Moreover, unlike in isotropic liquids where only short-range intermolecular interactions exist, the long-range interactions which characterize the nematic state lead in an ideal, nematic, single crystal to a uniaxial alignment of the long molecular axes along the nematic director $\hat{n}$. Therefore, macroscopic deformations can be imposed on the director $\hat{n}$ by external electric or magnetic fields, or by constraints imposed by forces resulting from the contact of the liquid crystal sample with its container walls. These deformations can be described by a mechanical continuum theory. From the theory follows for the distortion free energy F_d of the nematic director.[10]

$$F_d = \frac{1}{2}k_1 (\text{div } \hat{n})^2 + \frac{1}{2}k_2(\hat{n} \times \text{curl } \hat{n})^2 + \frac{1}{2}k_3(\hat{n} \times \text{curl } \hat{n})^2. \quad (1)$$

The constants k_i in equation (1) are associated with the three basic types of deformation which can be imposed on a nematic liquid crystal and which are depicted in Figure 4. They describe the elastic restoring forces splay (k_1), twist (k_2) and bend (k_3) which are—like the dielectric, optical and viscous properties—crucial for the operability and performance of liquid crystal displays.

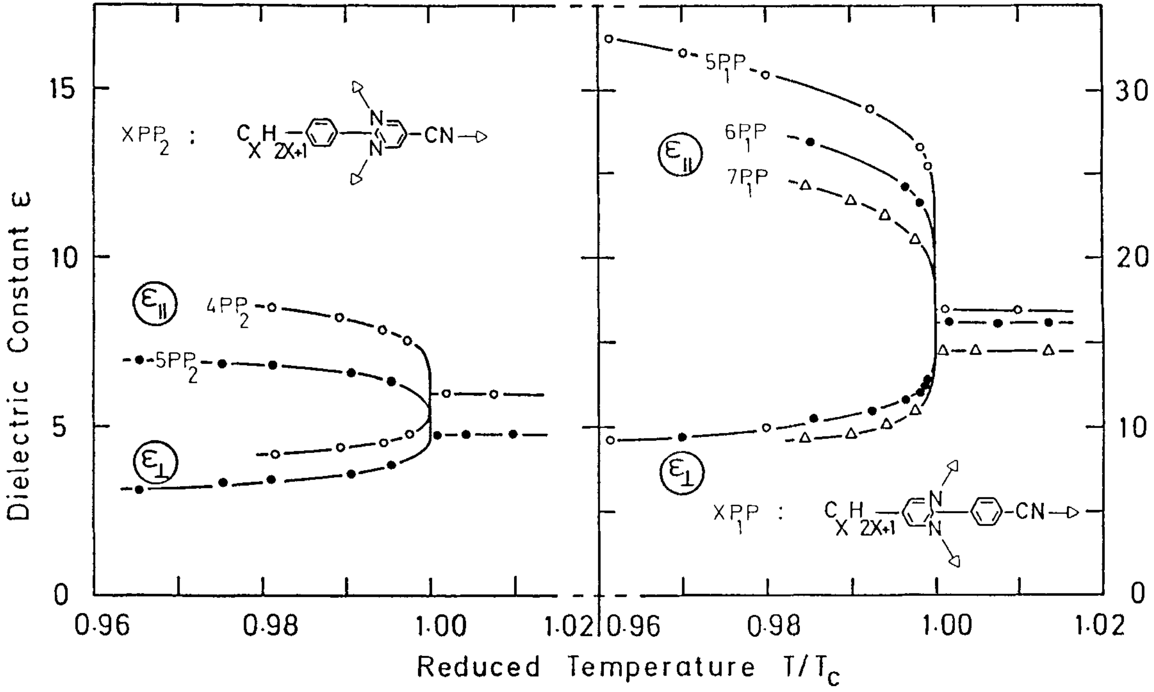


FIGURE 3 Static dielectric constants $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ of two different classes of pyrimidine liquid crystals versus reduced temperature T/T_c. Nomenclature: P_i = pyrimidine ring where i = 1,2 designates the position of the pyrimidine nitrogens, P = phenyl ring, X = number of carbon atoms in the alkyl side chain. The cyano end-group is not specifically indicated. At the first-order nematic-isotropic transition temperature $T = T_c$, the nematic anisotropies disappear, leading to $\Delta\epsilon = 0$ and $\Delta n = 0$.

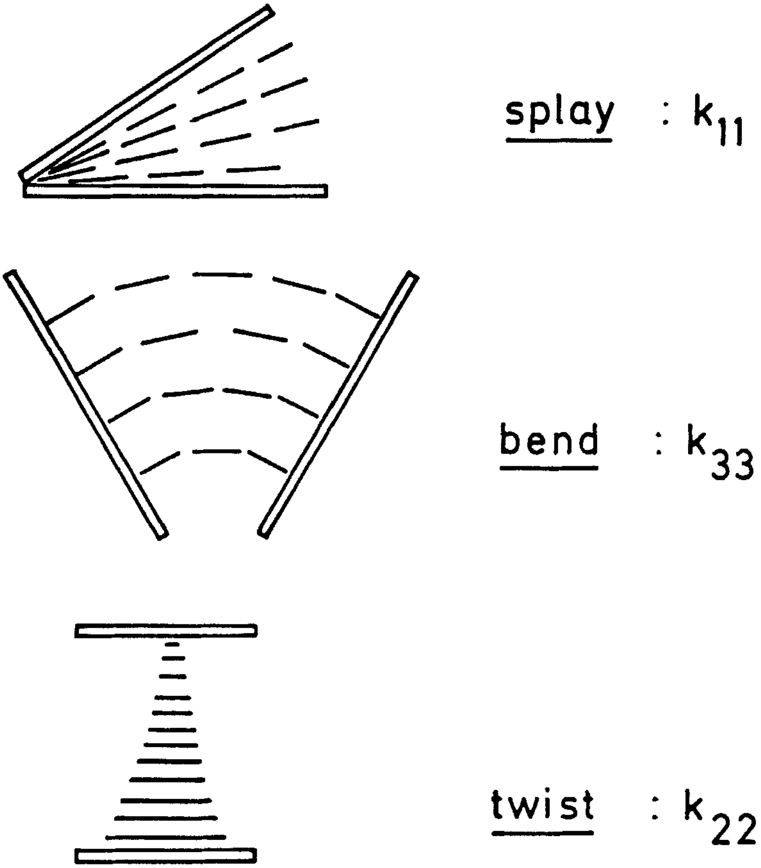


FIGURE 4 The three basic types of deformation that can be imposed on an ordered nematic liquid crystal layer lead to the splay (k_1), bend (k_3) and twist (k_2) elastic constants.

3. THE TWISTED NEMATIC EFFECT

Before the unique properties of liquid crystals can be visualized in displays, electro-optical effects have to be found which make them macroscopically visible. The operating principle of an applicable electro-optical effect has to be such that the optical appearance of a display based on the effect, reversibly changes upon applying an external voltage. The contrast between off- and on-state should be large. Moreover, the displays have to be competitive with alternative technologies, as for instance with light emitting diodes (LEDs), vacuum fluorescent displays (VFDs) or even with the high information content cathode ray tubes (CRTs). Therefore, the effect has to offer technological advantages such as full color reproducibility, low power consumption, large design flexibility, compatibility with low voltage and low power integrated driving circuits, flat design, reliability and the potential to be applicable in high information content displays such as in computer or television screens. The inherent drawbacks of an effect have to outweigh its advantages. Moreover, the LC-material parameters which the effect requires must be such that it is possible to design appropriate liquid crystal structures.

The twisted nematic (TN) effect[4] has proven to be suitable for realizing most of the above display requirements. The left of Figure 5 schematically shows the off-state of a positive contrast TN-LCD. Incident light which is linearly polarized by the entrance polarizer is rotated by the 90° twisted nematic configuration such that its polarization direction at the bottom cell boundary is parallel with that of

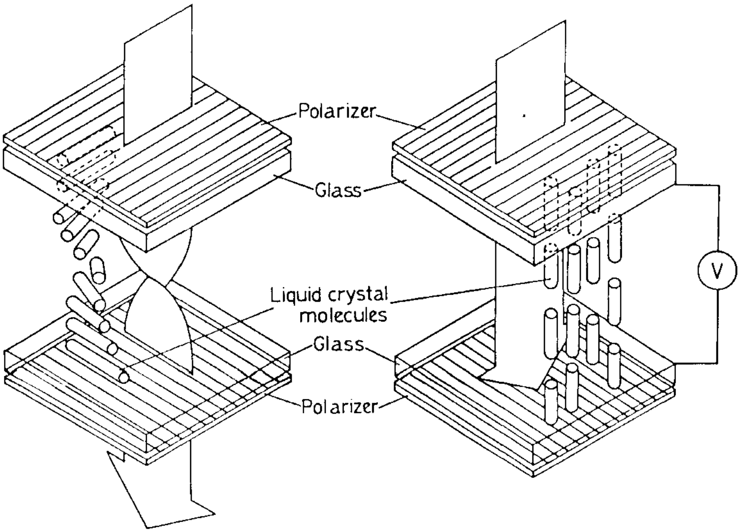


FIGURE 5 Operating principle of a positive contrast twisted nematic liquid crystal display (TN-LCD).[4] Figure a shows the helically-twisted off-state. The wall alignment of the LC-molecules which enforces the 90° twist is either achieved by angular evaporation of SiO_x[24] or by coating the transparent electrodes with polymer layers[25] which are rubbed parallel to the respective polarization directions of the adjacent polarizers prior to filling the TN-LCD. Because of waveguiding of the nematic helix, the crossed polarizer TN-LCD configuration is transparent in Figure (a). Figure (b) shows the on-state where the applied voltage V aligns the positive dielectric anisotropic LC-molecules parallel to the electric field. The nematic layer becomes optically uniaxial, therefore, the TN-LCD blocks light (positive contrast configuration). A negative contrast TN-LCD with a transparent on-state results if the two polarizers are aligned parallel.

the exit polarizer. As a consequence the crossed polarizer configuration of Figure 5 is transparent in the off-state. If a voltage is applied to the TN-LCD, the nematic director in the center of the twisted, positive dielectric anisotropic liquid crystal layer gradually aligns parallel to the electric field, that is, perpendicular to the electrode surfaces. To initiate this field-induced distortion requires—depending on the LC-material—a voltage of 1–2 volts to overcome the elastic restoring forces which stabilize the helical off-state configuration of the TN-LCD. At large voltages the alignment becomes virtually perpendicular to the electrode surfaces (Figure 5). An optically uniaxial nematic layer results which no longer rotates the polarization direction of incident, linearly polarized light. As a consequence the crossed polarizer configuration in Figure 5 becomes non-transmissive in the on-state. Aligning the two polarizers in Figure 5 parallel to each other reverses the contrast of the TN-LCD from positive to negative, that is, the off-state becomes non-transmissive and the on-state transmissive. For optical path differences

$$\frac{\Delta n \cdot d}{2\lambda} = 0.5, 1, 1.5, \ldots, \tag{2}$$

where d = cell gap and λ = wavelength of light,[11] virtually no elliptically polarized light is generated in the TN-LCD configuration of Figure 5. Therefore, the light dispersion is small in this so called wave guiding mode.[4,12] As a consequence, properly designed TN-LCDs exhibit very large contrast ratios between off- and on-state, which are limited only by the quality of the polarizers. Moreover, TN-LCDs appear black-white with gray levels at intermediate driving voltages. The black-white appearance allows to combine TN-LCDs with color filters such that the full range of colors of the visible spectrum can be reproduced by mixing the three basic colors. This is achieved by segmenting the bottom electrodes such that each picture element (pixel) consists of three individually addressable electrodes which are covered with selective color filters. In their projection the addressed segments distort the respective twisted nematic configurations such that the desired subtractive pixel color results.

From Figure 5 follows that TN-LCDs can be operated in transmission as well as in reflection. In reflection a diffuse reflector has to be mounted behind the rear polarizer, thus causing the incident light to pass the helix twice. Because TN-LCDs are passive displays they do not generate light like active LEDs or CRTs. Therefore, contrary to active displays the visibility of reflective TN-LCDs improves with increasing surrounding brightness. Because the optical signal of a TN-LCD is generated by merely realigning the nematic director by an electric field (field effect), thus modulating the intensity of externally available light, its power consumption is—with ~ $1\mu W/cm^2$—orders of magnitude smaller than that of any active display.

The desired electro-optical characteristics of a TN-LCD, which is determined by the LC-material parameters as well as by the surface aligning technology used, strongly depends on its application. If continuous attenuation of the transmitted light is required to generate gray levels between the white off- and the black on-state, rather flat electro-optical characteristics are desirable. On the other hand the reproduction of complex pictures or elaborate texts with passively addressed high information content TN-LCDs requires steep electro-optical characteristics. The upper part of Figure 6 shows the transmission versus applied voltage of a TN-LCD viewed at vertical light incidence ($\theta = 0°$) and at viewing angles $\theta = 10°, 20°, 40°$. The graphs show that TN-LCDs exhibit an optical threshold voltage below which the display is turned off. For $V > V_{90}$ the angular dependent transmission in Figure 6 decreases continuously (gray levels) until the non-transmissive (black) on-state is reached.

The turn-on time required for the twisted nematic configuration to become optically uniaxial upon applying a voltage depends essentially on the dielectric anisotropy, the elastic constants as well as on the viscosity of the liquid crystal material. Short turn-on times follow for large values of $\Delta\epsilon$, low viscosities γ and/or large applied voltages. Elaborate numerical calculations are required to describe the complex dynamic- and static electro-optics of TN-LCDs.[12] The recording at the bottom of Figure 6 shows typical turn-on and turn-off times of a TN-LCD upon applying a gated sine-wave voltage.

In $\varphi = 90°$ twisted TN-LCDs with zero bias tilt boundary layers (Figure 5) left and right hand helices are energetically equally favourable. As a consequence disinclination walls easily develop within the area of the LCD. They are due to reverse twist and/or reverse tilt domains.[13] To unambigously define the helical sense of the configuration in Figure 5 and to suppress reverse twist, either long pitch cholesteric additives can be added to the nematic LC such that $d/P >> 1$ results—where d = cell gap and P = induced helical pitch[14]—or the twist angle can be chosen $\varphi \neq 90°$. Reverse tilt and reverse twist are simultaneously suppressed by combining boundary aligning layers which induce small bias tilt angles with $\varphi \neq 90°$ twist configurations.[13]

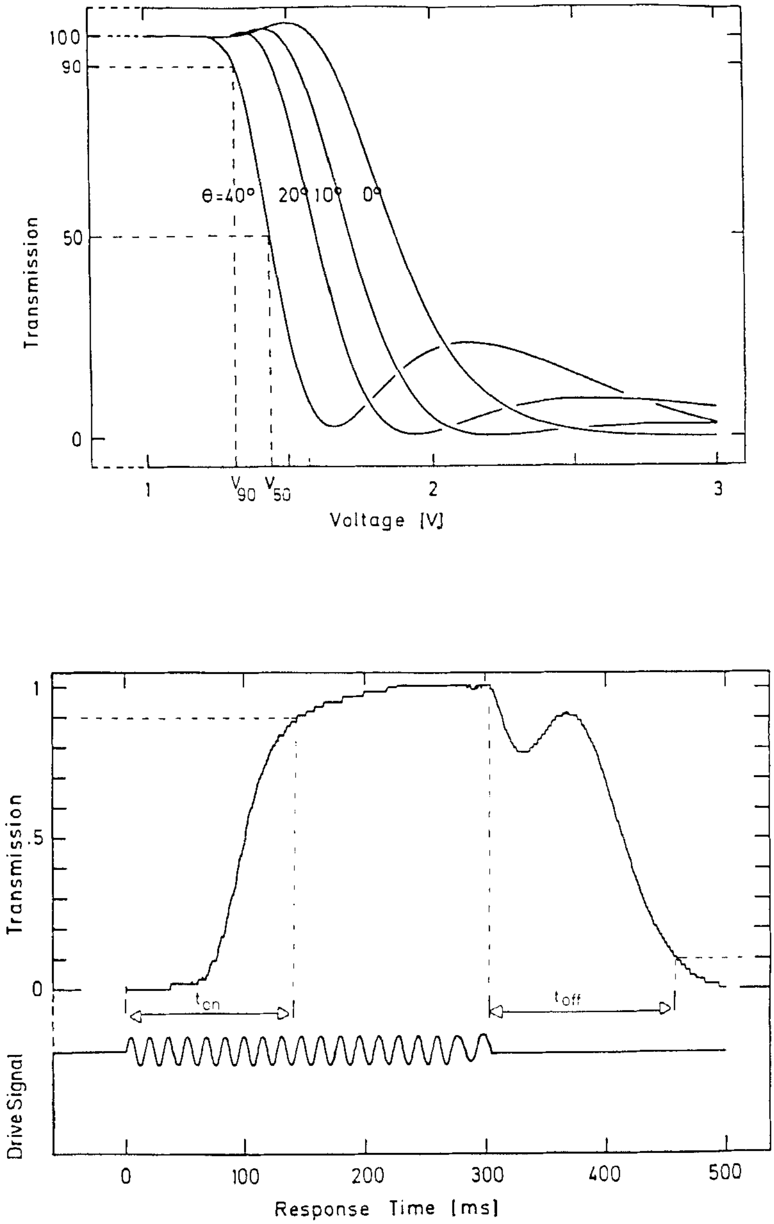


FIGURE 6 Top: Static transmission-voltage characteristics of a TN-LCD viewed at different angles θ. $\theta = 0° =$ vertical light incidence. V_{90} is the voltage required to obtain 90% transmission at a given viewing angle θ. Bottom: Optical response of a TN-LCD upon applying a gated sine wave voltage. t_{on} = time required to obtain 90% transmission; t_{off} = time required for the LCD to return to 10% transmission.

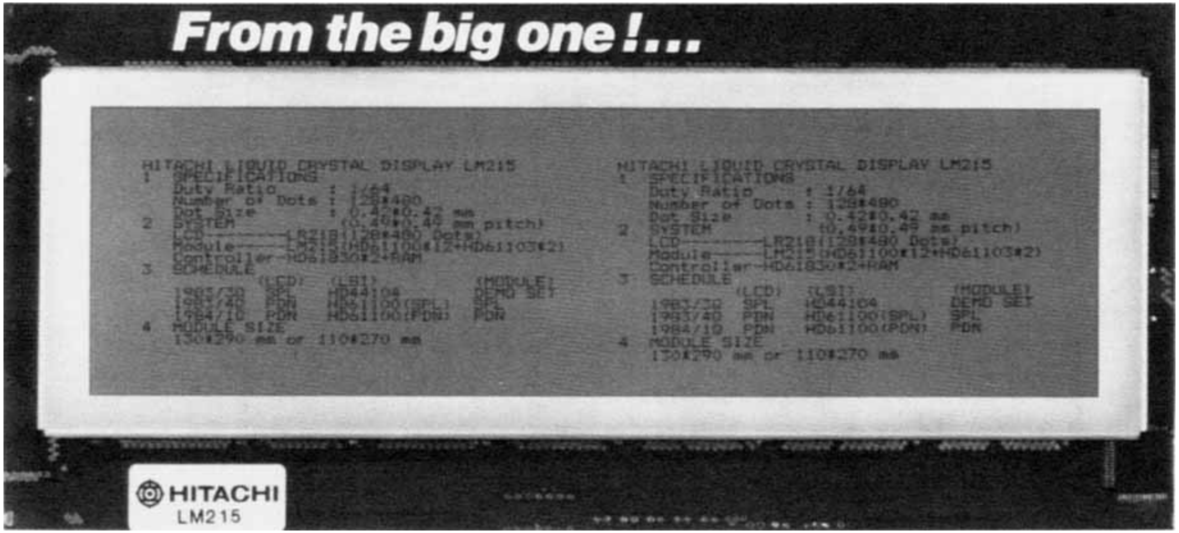
4. TIME MULTIPLEXING OF TN-LCDs

The complexity of TN-LCDs has been impressively increased since their first application in simple 3½ digital watch displays in 1972.[15] Currently available dot matrix TN-LCDs of the type shown in Figure 7 comprise about 100'000 pixels. To address each pixel of such a complex display via individual connections would be technologically impossible. Therefore, time multiplexed addressing techniques[16–18] were developed which make use of the specific electro-optical characteristics of TN-LCDs to significantly reduce the number of connections and driving integrated circuits.

Figure 8 shows the principle of time multiplexing. The display electrodes are no longer segmented like in simple, directly addressed, seven segment watch displays but are arranged in lines (upper substrate) and columns (lower substrate). Depending on the optical pattern to be generated, voltage pulses with different shape and amplitude are applied to the externally accessible electrodes of the TN-LCD matrix. In Figure 8 the normalized voltage pulses add up to potential differences of either 1 or 3 across the respective crossings of the electrode matrix. From the static transmission characteristics in the upper part of Figure 8 follows that for normalized voltages $V < V_{10} = 1$ no optical change occurs. Therefore, the crossings with $V = 1$ remain in the off-state, whereas those with $V = 3 > V_{10}$ are turned-on. The example shows that multiplexing allows significantly to reduce the number of connections of a TN-LCD matrix with N lines and M columns from (N × M) to (N + M). Prerequisites are a well defined threshold voltage over as wide as possible a viewing range, steep enough voltage-transmission characteristics and a small temperature and viewing angle dependence of the characteristics. With flat characteristics the contrast ratio between off- and on-state decreases with increasing multiplexing ratio N_{max}; where N_{max} = maximum number of multiplexible lines. For a given steepness of the characteristics defined by the slope parameter p (Figure 8), follows for N_{max}:[16]

$$N_{max} = \frac{[(1 + p)^2 + 1]^2}{[(1 + p)^2 - 1]^2}. \tag{3}$$

Equation (3) shows that the multiplexibility and therefore the attainable complexity of a display increases with decreasing slope parameter p. For $p = 0$ an infinite number of lines can be multiplexed with a contrast as large as that of a directly addressed display.



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HITACHI LIQUID CRYSTAL DISPLAY LM215
1   SPECIFICATIONS
    Duty Ratio      : 1/64
    Number of Dots  : 128*480
    Dot Size        : 0.42*0.42 mm
2   SYSTEM            (0.49*0.49 mm pitch)
    LCD-----------LR218(128*480 Dots)
    Module--------LM215(HD61100*12+HD61103*2)
    Controller-HD61830*2+RAM
3   SCHEDULE
           (LCD)   (LSI)              (MODULE)
    1983/30  SPL   HD44104            DEMO SET
    1983/40  PDN   HD61100(SPL)       SPL
    1984/10  PDN   HD61100(PDN)       PDN
4   MODULE SIZE
    130*290 mm or 110*270 mm
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3   SCHEDULE
           (LCD)   (LSI)              (MODULE)
    1983/30  SPL   HD44104            DEMO SET
    1983/40  PDN   HD61100(SPL)       SPL
    1984/10  PDN   HD61100(PDN)       PDN
4   MODULE SIZE
    130*290 mm or 110*270 mm
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FIGURE 7 64:1 multiplexed dot matrix TN-LCD. **See Color Plate VI.**

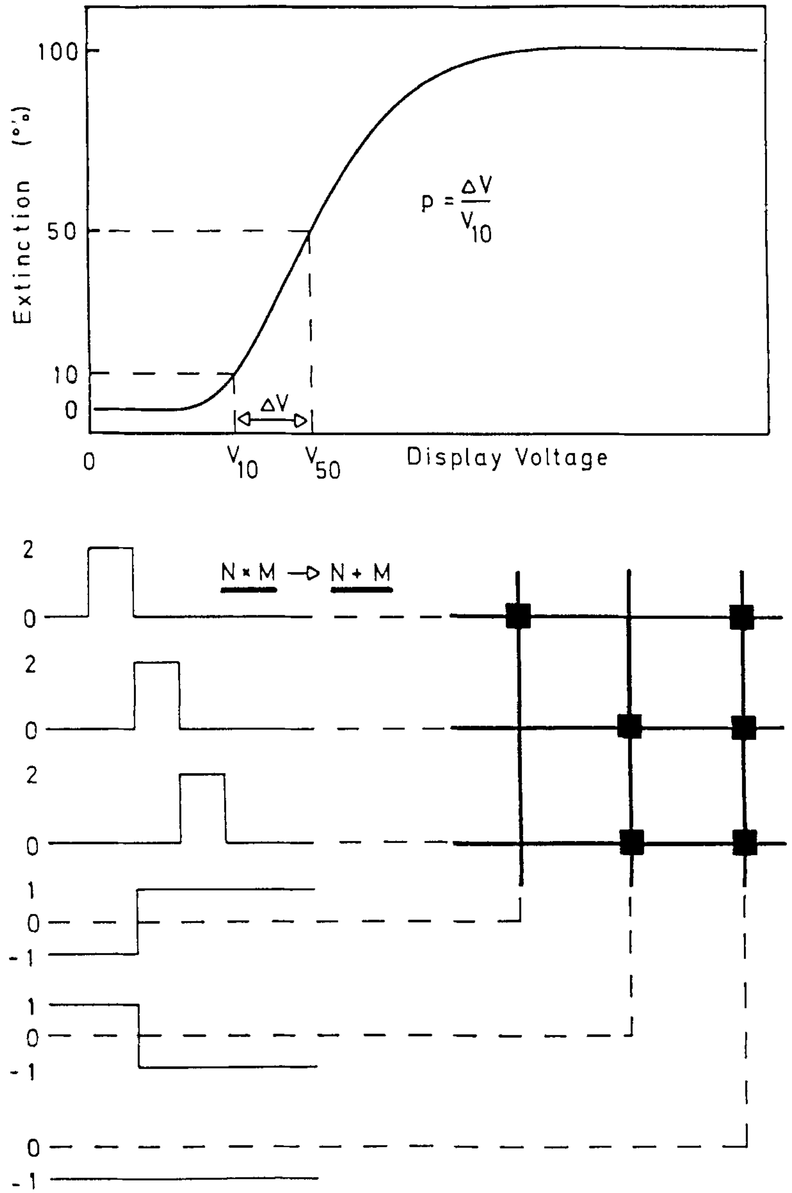


FIGURE 8 Top: Transmission-voltage characteristics of a TN-LCD. The slope parameter p characterizes the steepness of the characteristics; it is defined by $p = (V_{50} - V_{10})/V_{10}$. Bottom: Matrix array of N lines and M columns of the electrodes of a matrix addressable TN-LCD. The black squares are the on-pixels of the matrix, that is, those electrode crossings where the amplitudes of the applied voltage pulses are $V = 3 >> V_{10}$.

5. DEPENDENCE OF THE ELECTRO-OPTICAL PROPERTIES OF TN-LCDs ON LIQUID CRYSTAL MATERIAL PARAMETERS

It was not until the early 1980s that all experimental techniques, especially those to measure elastic constants reliably,[19] were developed and used to find correlations between all relevant material parameters of different liquid crystal structures and their influence on the electro-optical performance of TN-LCDs.[20,21] At the same time attempts were made to find approximations to describe the complex static electro-optical performance[12] of TN-LCDs by physically meaningful analytical expressions.[20] For the driving voltage V_{50} required to obtain 50% transmission in a low bias tilt TN-LCD at vertical light incidence, the following approximation was obtained:[20]

$$V_{50} \cong V_c \times \left[2.044 - \frac{1.044}{1 + k_3/k_1}\right] \times \left\{1 + 0.123\left[\left(\frac{\Delta\epsilon}{\epsilon_\perp}\right)^{0.6} - 1\right]\right\} \times \left(1 + 0.132\, ln\frac{\Delta n d}{2\lambda}\right). \quad (4)$$

where V_c is the threshold voltage for the mechanical deformation of the helix of the TN-LCD:

$$V_c = \pi\left[\frac{1}{\epsilon_0\Delta\epsilon}\left\{k_1 + (k_3 - 2k_2)\left(\frac{\varphi}{\pi}\right)^2\right\} + 2k_2\left(\frac{\varphi}{\pi}\right)\frac{2d}{\mathrm{P}}\right]^{1/2}. \quad (5)$$

In (5) P is the natural pitch of the nematic liquid crystal doped with a chiral additive, φ = twist angle and d = cell gap. For a purely nematic material where P = ∞ and for a TN-LCD with $\varphi = 90°$ twist, follows from (4) and (5) that V_{50} mainly depends on the dielectric anisotropy $\Delta\epsilon$ and on the elastic expression $\kappa = [k_{11} + (k_{33} - 2k_{22})/4]$. Increasing $\Delta\epsilon$ and/or decreasing κ reduces the operating voltage.

At vertical light incidence the steepness of the static transmission characteristics of a TN-LCD can be approximated by:[20]

$$p = (V_{50}/V_{10} - 1) \propto a + b(k_{33}/k_{11} - 1) + c\left(\ell n\frac{\Delta n d}{2\lambda}\right)^2. \quad (6)$$

where a, b, and c are constants depending on the cell technology. From (6) follows that steep characteristics and therefore large multiplexing ratios (Equation 3) result for LC-materials with small bend/splay elastic ratios k_{33}/k_{11} and operation of the LCD in the second transmission minimum, where $\ell n(\Delta nd/2\lambda) = 0$ holds (Equation 2)

Not only the static electro-optical performance of TN-LCDs crucially depends on LC-material parameters but also their dynamics. This is shown for the decay time t_{off} at small angles of helix deformations by:[22]

$$t_{\text{off}} \propto \gamma_1/\kappa, \tag{7}$$

where γ_1 = rotational viscosity of the LC-material. From Equation (7) follows that short turn-off times not only require low viscous LC-materials, their elastic constants should also be such that the elastic expression κ becomes large. If such materials can be realized, synergetic effects and consequently much shorter turn-off times can be achieved than with low viscous materials alone.

6. MOLECULAR STRUCTURES AND LC-MATERIAL PARAMETERS

The previous paragraph shows that specific LC-material properties are required to achieve a good overall performance of a liquid crystal display. The requirements are different for different electro-optical effects. They are also different for different applications of the display. Therefore, molecules exhibiting the desired physical properties have to be developed. However, even the best single components possess only one or two outstanding properties. To achieve nevertheless an optimal electro-optical performance within the range of components from the best liquid crystal classes known at a given time, complex LC-mixtures comprising up to twenty components have to be designed. This allows to optimize the more than ten different LC-material parameters determining the LCD performance for a given application.[23] A prerequisite for good overall material properties are therefore single components which excell in one or more respects and the design of mixtures such that the favorable component properties become dominant, whereas the unfavorable ones are suppressed.

6.1. Technologically important liquid crystal classes

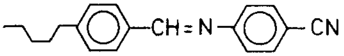
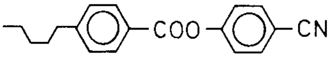
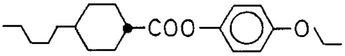
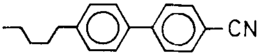
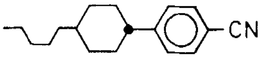
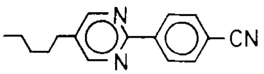
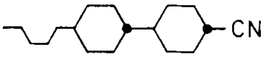
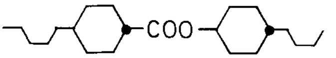
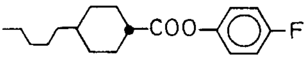
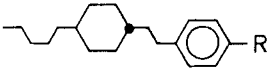
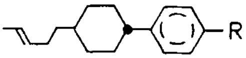
The development of the LCD technology is closely related with the progress made in LC-materials since the early 1970s. Modern LC-mixtures comprise molecules which belong to different liquid crystal classes. Each class consists of structurally similar molecules exhibiting class-specific physical properties.[20] Therefore, one crucial prerequisite for improving the performance of LC-mixtures is to design molecules with improved structures. The intention is not to review in this paragraph the large number of interesting and important LC-classes that were developed to achieve the high levels of performance of today's LCDs. Only representatives of the few LC-classes which essentially contributed to this development and whose performance justified manufacturing are chronologically listed in Table I.

The Schiff's bases on top of Table I were the first positive dielectric anisotropic nematics that were developed to promote the commercialization of TN-LCDs after the twisted nematic effect was discovered in 1971.[4] They were the first to exhibit wide enough mesomorphic phases and low enough operating voltages to be applicable in commercial watch and instrument TN-LCDs.[15] However, because of hydrolysis of the Schiff'base linkage —CH=N— in contact with humidity, Schiff'bases could only be used in water tight, glass-frit sealed displays. Therefore, and because high temperature, glass-frit sealing processes require angular evaporation of SiO_x to achieve the planar wall alignment[24] in TN-LCDs, these first generation nematics could no longer be used in the low temperature processed, polymer aligned[25] and plastic sealed TN-LCDs developed by the Japanese display industry in the mid 1970s. For these displays, the cyano biphenyls, which were discovered in 1974,[26] and to a lesser extent also the cyano esters,[7] proved to be much more compatible. Therefore, and because of the lower viscosities of cyano biphenyls compared with Schiff'bases, biphenyls became successful in subsequent generations of LC-mixtures designed for epoxy sealed and polymer aligned TN-LCDs.

With increasing sophistication of the TN-LCD technology the LC-material requirements, especially towards shorter response times, wider mesomorphic temperature ranges, lower operating voltages, multiplexibility, etc. became more and more demanding; a trend that will go on as long as the large potential of the technology has not been exhausted. Thus, another important improvement, especially towards shorter response and wider mesomorphic temperature ranges was the discovery of the cyanophenylcyclohexanes[29] (PCHs) in 1977 (Table I). With PCHs it became possible to develop for the first time, wide temperature range mixtures for automotive applications with sufficiently short response times at −30°C. At about the same time the first heterocyclic polar nematics[28] ($5P_1P$ in Table I) were developed which greatly contributed to the improvement of the multiplexibility of high information content TN-LCDs.[20,23] However, nei-

TABLE I

Representatives of some two-ring LC-classes which strongly promoted the TN-LCD technology. Except for the abbreviations in brackets the nomenclature used is: C = cyclohexane ring, P = phenyl ring, P_1 = pyrimidine ring, E = ester, A = ethane, Xd_y = alkenyl double bond with y defining its position in the side chain. The respective numbers X preceeding d_y or a ring indicate the number of carbon atoms in the attached alkyl side chain.

NOMENCLATURE	STRUCTURE	YEAR	REF.
(S5)		1972	(7)
5PEP		1972	(15)
5CEPO2		1973	(8)
5PP (K15)		1974	(26)
5CP (PCH5)		1977	(27)
5P_1P		1977	(9)
5CC		1978	(29)
5CEC4		1979	(30)
5CEPF		1981	(34)
5CAPR		1982	(31-33)
1d_3CPR		1985	(35-38)

ther the components of any of the above LC-classes nor combinations of them exhibit all of the desired properties. To push the technological limits further, new and still more sophisticated LC-classes were and still are required. Thus, the bicyclohexanes[29] (5CC in Table I) and the bicyclohexane esters[30] (5CEC4 in Table I) contributed to lowering the optical anisotropy of mixtures such that operation of TN-LCDs became feasible in their first transmission minimum (Equation 3), i.e. at technologically accessible not too small cell gaps. A further step towards still shorter response times was achieved with the ethanes[31-33] and with the fluorinated esters[34] (Table I). The introduction of double bonds into side chains led to a large number of new liquid crystal classes (alkenyls) which for instance considerably enlarged the range of elastic properties of LC-materials.[35,36] Moreover, in combination with different rigid cores, alkenyls often exhibit a better over-all performance than their saturated counterparts.[37]

6.2. Material properties and alkenyl structures

In the following some alkenyl liquid crystals which were recently developed in our laboratories[35-38] and relations between their structures and material parameters are presented as examples of the design of modern LCs. Figure 9 schematically shows our approach: from investigations of correlations between LC-structures and their material parameters result structures with specific physical properties and leads for new structures. Investigations of electro-optical effects on the other hand are a prerequisite for finding those material parameters which are crucial for a given electro-optical effect; they can also lead to the discovery of new effects. The arrows pointing at different positions of the LC-structure in Figure 9 indicate the systematic changes which we made in case of alkenyls on (i) the right hand substituent (ii) the rings and their linkage and (iii) the position of the alkenyl double bond in the side chain(s). The proper combination of structural elements has led to a number of synergetic improvements.[35-38]

Figure 10 shows the temperature dependence of the bend/splay elastic ratio k_3/k_1 for two-ring nematic compounds with different polar end groups; rigid cores with different rings as well as saturated and non-saturated side chains.[35-37] Comparing the saturated phenyl cyclohexane 5CP[27] in Figure 10 with the alkenyl phenylcyclohexane $1d_3$CP it is evident that the introduction of a double bond d in 3-position (d_3) strongly increases k_3/k_1. On the other hand, shifting the double bond one position further away from the rigid core leads to

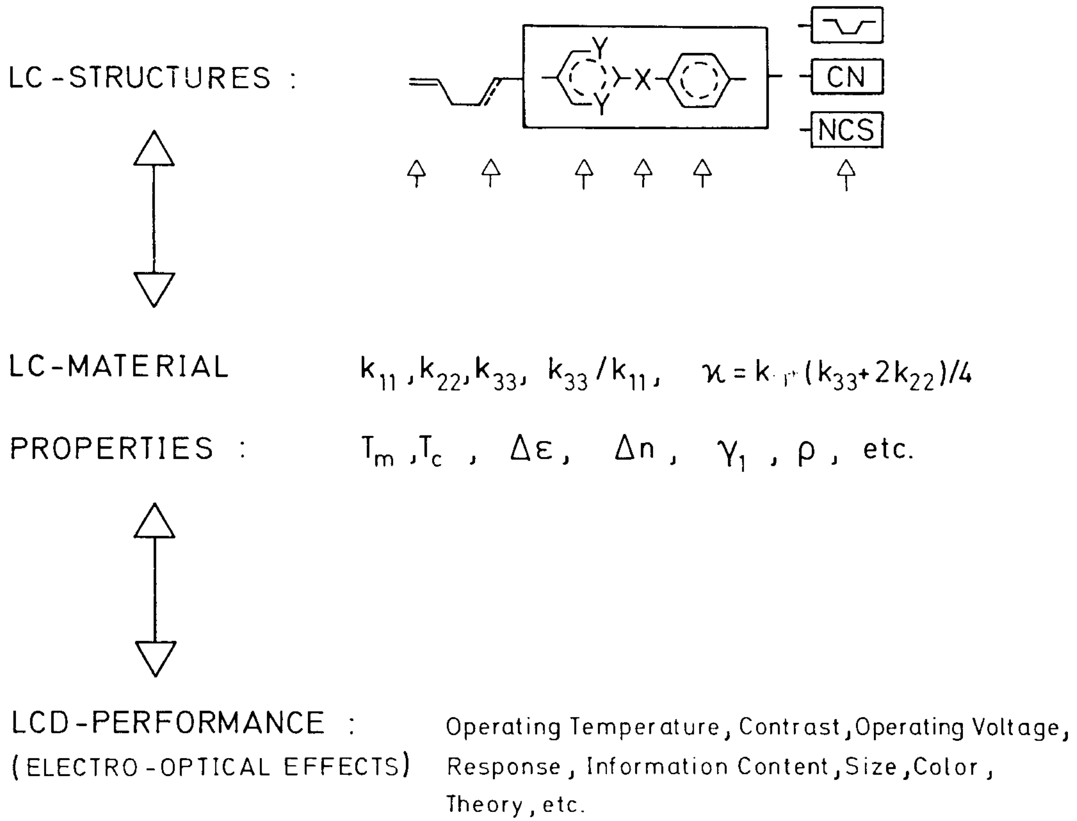


FIGURE 9 Example of our design principle for liquid crystals in case of alkenyls: molecular structural elements are related via LC-material parameters with their electro-optical performance in displays.

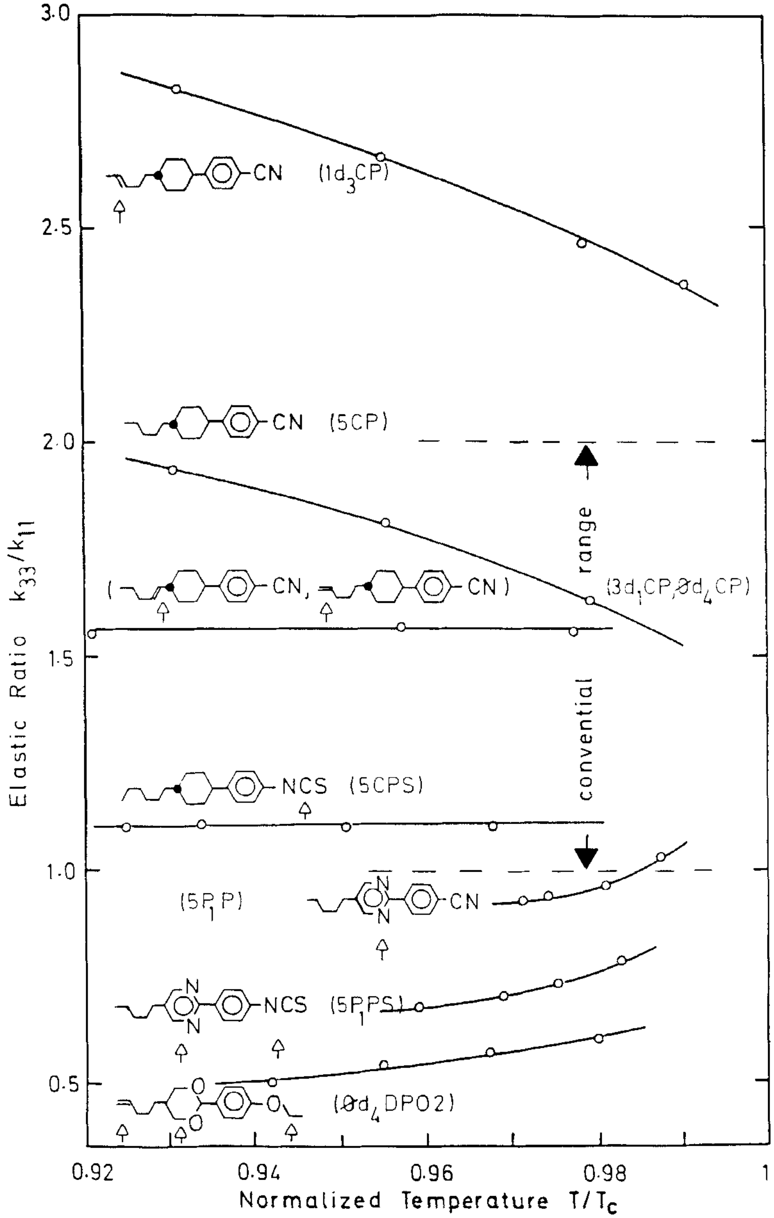
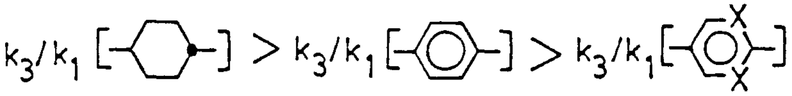


FIGURE 10 Temperature dependence of the bend/splay elastic ratio k_3/k_1 of different liquid crystal classes. Nomenclature: Xd_i = double bond at i-position from the rigid core; X = number of carbon atoms attached to the double bond, or, in case of saturated side chains: number of carbons in the chain; C = cyclohexane ring; D = dioxane ring; S = NCS. ($3d_1$ CP, $0d_4$CP) = (60% mol, 40%) = binary mixture. The arrows indicate the systematic structural changes made.

the alkenyl ϕd_4CP which exhibits a markedly reduced elastic ratio k_3/k_1 (Fig. 10). The example shows that introducing a double bond in specific side chain positions strongly affects k_3/k_1. In odd positions the ratio increases, whereas even positions cause a reduction of k_3/k_1.

We have shown that k_3/k_1 not only depends on the structure of the side chain within structurally comparable molecules but also on the type of rings used in their rigid cores.[20] k_3/k_1 decreases in the following order:



Thus, heterocyclic rings, such as pyrimidine or dioxane rings, lead to low k_3/k_1 values (Fig. 10), whereas cyclohexane rings increase this ratio. k_3/k_1 also decreases within a given LC-class when reducing the polarity of the molecules, that is, their dielectric anisotropy.[20] Moreover, as the comparison between the CN— and the NCS structures in Figure 10 shows, k_3/k_1 is also affected by the type of polar end groups used.[36]

From the above, synergetic effects can be expected to occur when properly combining different structural elements. This is illustrated by the nonpolar 4-alkenyl dioxane ϕd_4DPO2 at the bottom of Figure 10. Its very low k_3/k_1 ratio is due to the combination of 4-alkenyl side-chain, heterocyclic ring and nonpolar alkoxy side-chain. Because of its low k_3/k_1 ratio and from equation (6) follows that ϕd_4DPO2 leads to steep transmission-voltage characteristics in mixtures designed for multiplexing TN-LCDs.

The above correlations have made it possible to design molecules which not only disprove the simplistic assumptions of fixed elastic ratios, such as $k_{11} = k_{22} = k_{33}$,[6] often used in liquid crystal mean field theories; moreover, they extend the range of elastic ratios of liquid crystals by almost a factor of three compared with the "conventional" range (Fig. 10).

Changing the position of the alkenyl double bond affects not only the elastic ratios k_3/k_1 of liquid crystals but other material properties as well. This is demonstrated in Figure 11 by the alkenyl isothiocyanates with different positions of terminal double bonds.[36,38] From Figure 11 follows that the dielectric, the optical and the elastic properties of alkenyl liquid crystals strongly depend on the double bond position. Pronounced odd-even effects result, leading in even posi-

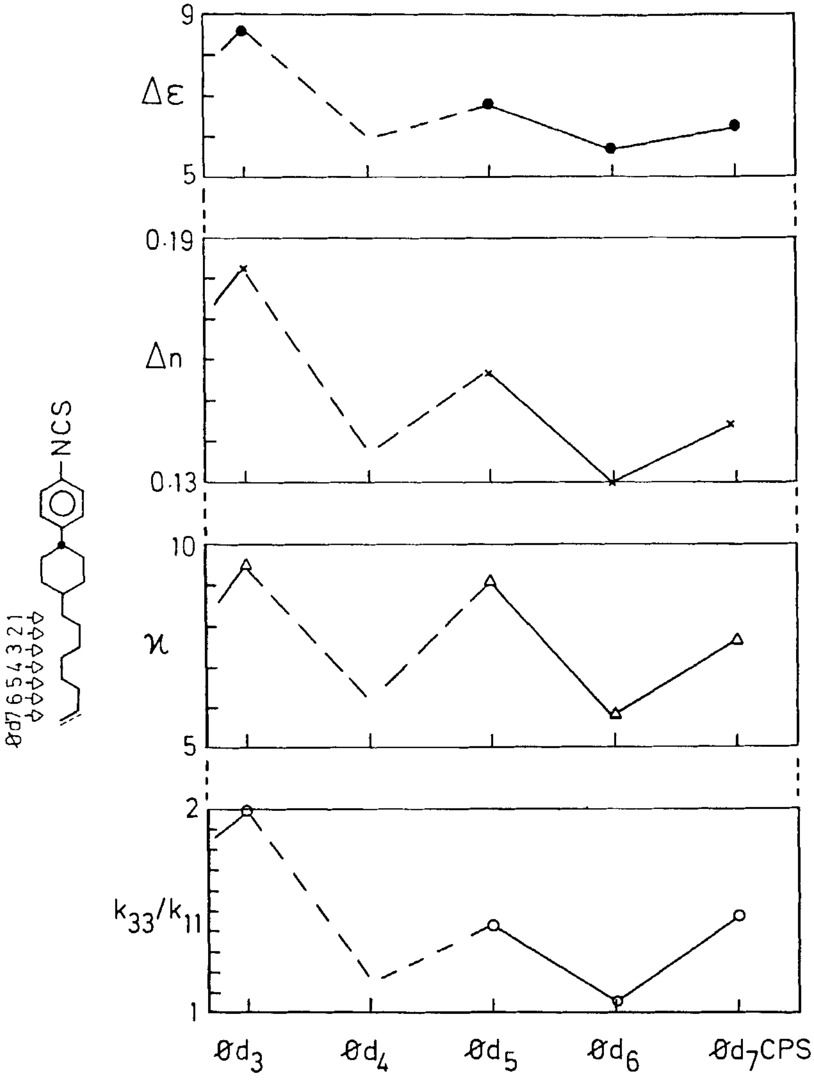


FIGURE 11 Odd-even effects that occur when changing the position of the double bond in Xd_iCPS alkenyls. Odd-positions lead to large elastic, dielectric and optical material constants, whereas even positions strongly reduce those constants; $\kappa = k_1 + (k_3 - 2k_2)/4$.

tions to low values of the material constants (Fig. 11), whereas large values result for odd positions. As a consequence and from the above approximations (eq. 4–7) it follows that in the case of TN-LCDs it is not only the slope p of their transmission characteristics that is affected by the position of the double bond (via k_3/k_1) but also their threshold voltage V_{10} (via $\Delta\epsilon$ and κ) and their response time t_{off} (via κ and γ_1).

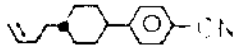
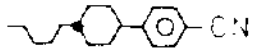
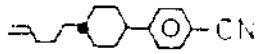
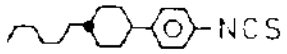
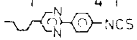
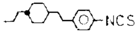
Table II summarizes some material properties of new polar LC-structures from our laboratories and relates them with their threshold voltage and turn-off times in TN-LCDs. As saturated reference compounds 5CP[27] and 6CPS[39] are included. Comparing in Table II the binary mixture on top which comprises 0d_3CP, with the third from the top, comprising 0d_4CP, shows not only markedly different mesomorphic temperature ranges of the two mixtures but also strongly different elastic and viscous properties. Thus, mainly because of the low κ-values of 0d_4CP its threshold voltage V_{10} is much smaller than that of 0d_3CP (Table II, eq. (7)). Moreover, Table II shows that the response time of the mixture with 0d_4CP is much slower than that with 0d_3CP, this despite the smaller rotational viscosity γ_1 of the former. The reason for this apparent discrepancy is the considerably larger elastic expression κ of 0d_3CP which—in accordance with equation (7)—efficiently contributes to shortening the response of TN-LCDs. This example illustrates that as a consequence of the improvement of one display parameter—lowering the threshold voltage—another parameter often deteriorates.

7. FUTURE DEVELOPMENTS

The progress made in liquid crystal materials and display technology has led to the development of TN-LCDs from simple, directly driven, small, digital watch displays into multiplexible, high information content displays, as well as into large area displays. Most of the LCD manufacturing processes used today are based on glass substrates; however, attempts are being made to replace glass by plastic materials. The advantage of plastic TN-LCDs[40] are: flexibility, virtually "paper flat" design, continuous attenuation of incident light without loss of imaging quality when used as optical shutters or in window applications and the possibility to use continuous production processes. However, since the diffusion of impurities through plastic substrates into the LC-layer is much more pronounced than with glass

TABLE II

Material properties of different liquid crystal classes comprising saturated and non-saturated side chains. The compounds marked *x* are binary mixtures with (60%, 40%) molar proportions. Binary mixtures are used to obtain in all cases sufficiently overlapping nematic phases. T_m = melting temperature, T_c = clearing temperature, k_3/k_1 = bend/splay elastic ratio, $\kappa = k_1 + (k_3 - 2k_2)/4$, γ_1 = rotational viscosity, V_{10} = TN-LCD threshold voltage and t_{off} = turn-off time in TN-LCDs with d = 8 μm cell gap.

LC		T_m	T_c	k_{33}/k_{11}	κ	$\Delta\varepsilon$	Δn	V_{10}	γ_1	t_{off}
		(°C)	(°C)		($\times 10^{-12}$N)			(volts)	(cP)	(ms)
(0d$_3$CP, 1d$_3$CP) 	x	38	65	2.56	10.9	12.4	0.127	1.9	150	32
5CP 		30	55	1.73	7.0	10.3	0.100	1.5	128	43
(0d$_4$CP,3d$_1$CP) 	x	5	35	1.53	5.4	10.8	0.105	0.8	97	67
6CPS 		13	43	1.10	9.1	6.9	0.137	1.6	83	41
(5P$_1$PS,0d$_4$P$_1$P,4P$_1$P) 	x	5	35	0.65	7.7	21.2	0.193	0.7	102	78
0d$_3$CPS 		25	43	2.00	9.5	8.6	0.183	1.8	51	17
(3CAPS,5CAPS) 	x	10	44	1.63	12	8.1	0.163	2.0	105	21
		measured at: (T_c -10°C)							22°C	

substrates, great care has to be taken especially in the design of new outdoor devices, such as large area, electrically controllable windows.

In our age of electronic communication, the demand for lightweight, flat displays, capable of reproducing high quality, complex, monochrome as well as color images is very strong. Technologically there are essentially two different approaches to realizing such high information content displays with LCDs. One is to further improve the multiplexibility of LCDs. The other is to develop actively addressed LCDs, that is, LCDs whose pixels are individually addressed by semiconductors integrated into each segmented electrode of a matrix type TN-LCD. The semiconductor elements consist either of amorphous thin film transistors (TFTs)[41,42] or of metal-insulator-metal (MIM)[43] diodes. Instead of with TN-LCDs, actively addressed display substrates can also be combined with guest-host (GH)-LCDs,[44-47], provided GH-liquid crystal systems and dichroic dyes with the required high specific resistivity ($\rho > 10^9$ Ohm.m) and stability will be achieved. The great advantages of actively addressed LCDs over passively addressed, time multiplexed LCDs, are the combination of fast response, high contrast and the capability to reproduce many gray levels. These advantages follow from the direct addressing of each pixel by an individual transistor, thus allowing to circumvent the time multiplexing problem described above. The electro-optical characteristics of the LC-materials required for TFT TN-LCDs are—except for their extremely large specific resistivity—essentially the same as those for sophisticated, non-multiplexed TN-LCDs. However, because grey levels are a prerequisite for achieving full color reproduction with TN-TFT-LCDs, LC-materials with large bend/splay elastic ratios, such as those of 3-alkenyls (Fig. 10), are required. TFT-LCDs stand a good chance to challenge successfully the dominant role of today's CRT television picture tubes not only in small size TV applications but also in high resolution,[48] large area projection TV systems.

Because of the complexity of TFT-LCDs and since computer terminals and other high information content applications often do not require the fast response or the full color reproduction of expensive TFT-LCDs, highly multiplexible LCDs remain of strong interest for all those applications which do not require the short reponse times and the large gray scale reproducibility of TV-screens. To display the high information content of A4-size LCDs with 400 × 620 lines and columns without active addressing but still with good optical quality, requires time multiplexed LCDs with steeper electro-optical characteristics than those attainable with TN-LCDs. Recently several groups have discovered electro-optical supertwist configurations with remarkably steep characteristics. They are the bistable, but low contrast guest-host effect by Waters et al.,[49] the high contrast supertwisted (STN) LCD by Kando et al,[50] the high contrast, superbirefringence twisted effect (SBE) by Scheffer and Nehring[51] and the optical mode interference effect (OMI) by Schadt and Leenhouts[52] and later on by Kawasaki et al.[53] Both STN and SBE LCDs depend strongly on the electrically tunable, large optical path difference $\delta = (n_e - n_o),d = \Delta n.d$ of the respective LC-configuration. Therefore, both exhibit strong interference colors in either on or off-state; black-white images are not possible in single layer configurations. Moreover, both require very precise cell spacing d, with gap variations in the tenth of a micrometer range, as well as LC-materials with a low operating temperature dependence of the optical anisotropy; i.e., with high nematic-isotropic transition temperatures. Besides, SBE-LCDs require large bias tilt angles at the cell boundaries. These limitations can be overcome with OMI-LCDs which exhibit at the same high level of multiplexing at least the same contrast and wide range of view. Moreover, the response of OMI-LCDs is faster, the dependence of their electro-optical characteristics on cell spacing much smaller and due to their low inherent coloration, black-white images and—in combination with color filters—full color images can be realized.[52,53]

Figure 12 shows the off-state of a transmissive OMI-LCD.[52] The $\varphi = 180°$ helical twist of the nematic helix in Figure 12 is achieved by doping the nematic LC with a cholesteric additive such that a natural helical pitch $\pi/2 < \varphi < 3\pi/2$ results. The precise twist angle is locked-in by wall aligning the nematic directors $\hat{n}_1$, $\hat{n}_2$ at the respective cell boundaries (Figure 12). For comparisons Figure 13 summarizes the configurations of TN-LCDs, STN-LCDs, SBE-LCDs and OMI-LCDs. Increasing the twist angle φ of OMI-LCDs leads to still steeper characteristics and to a brighter off-state.

Figure 14 shows recordings of the positive contrast transmission-voltage characteristics of the OMI-LCD at three different angles of view θ (solid graphs). For comparison the characteristics of a TN-LCD, operated in the first minimum are included (dashed graphs). Figure 14 shows that the OMI-LCD exhibits a pronounced threshold, much steeper electro-optical characteristics than TN-LCDs, as well as a smaller shift of the characteristics versus viewing angle. At vertical light incidence ($\theta = 0°$) follows from Figure 14 the slope parameter $p = (V_{50}/V_{90} - 1) = 0.032$ for the OMI-LCD. According to equation (3) this leads to a theoretical multiplexing ratio $N_{max} = 1000$ lines! For comparison, the corresponding values for the TN-LCD in Figure 14 are $p = 0.172$ and $N_{max} = 40$.

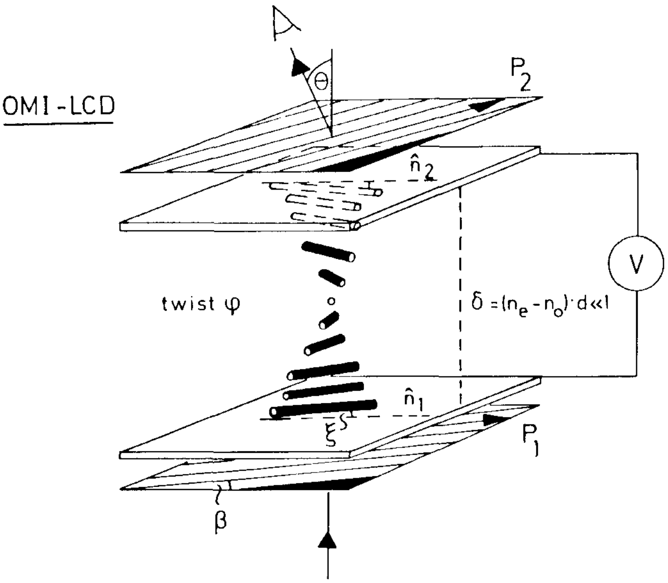


FIGURE 12 Schematic drawing of the off-state of a transmissive OMI-LCD. β = angle between polarizer direction P_1 and nematic director n_1, φ = twist angle, ψ = angle between P_1 and P_2, θ = angle of view and δ = $\Delta n.d$ = optical path difference of LC layer.

The above example shows that the OMI configuration not only leads to extraordinarily steep characteristics but also to a small angular dependence. These properties—in combination with its other features such as its black-white appearance and its small cell gap dependence—make the OMI effect an interesting candidate for realizing future, highly multiplexed, monochrome or color LCDs. Since—contrary to TN-LCDs—OMI-LCDs require LC-materials with large elastic ratios k_3/k_1,[54] alkenyls with odd double bond positions (Figures 10, 11) will lead to a still further improved multiplexibility in future OMI-LCDs.

To conclude, Table III summarizes some of the applications which are realized today or which can be expected to be realized within the next years with liquid crystal displays. Despite being far from complete, the table indicates the remarkable progress which has been achieved since the early 1970's when the TN-LCD technology started. It also shows the great potential of this young technology when it comes to realizing future, still more complex applications. A potential whose practical realization, like in the past, depends crucially on the close collaboration between physicists, chemists and electronics en-

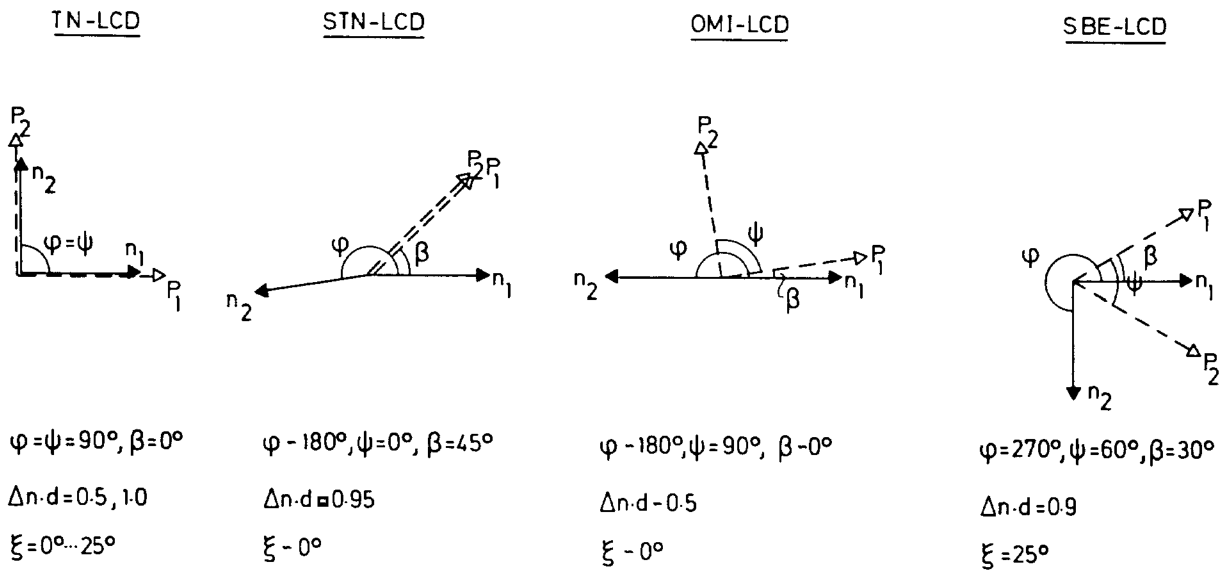


FIGURE 13 Typical configurations of polarizers P_1,P_2 and nematic directors n_1, n_2 in TN-LCDs,[4] STN-LCDs,[50] OMI-LCDs[52] and SBE-LCDs.[51] φ = twist angle, ψ = polarizer angle, β = angle (n_1, P_1), ξ = tilt angle of long molecular axes at surface boundaries and $\Delta n.d$ = optical path difference of LC-layer.

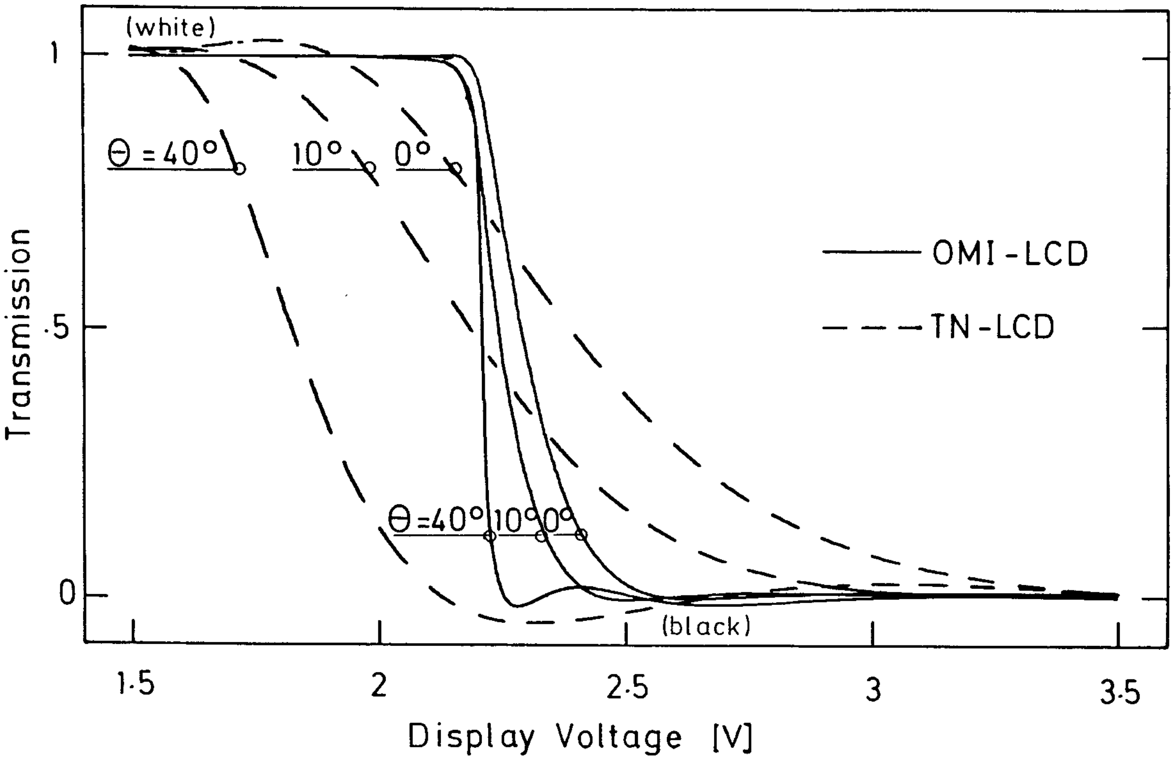


FIGURE 14 Transmission-voltage characteristics of OMI-LCD (solid graphs) and 90° TN-LCD (dashed groups) versus angle of view θ at 22°C comprising mixture 4244 from Roche.[54] The OMI configuration used is $\beta = 0°$, $\psi = 90°$, $\varphi = 180°$, $\delta = 0.465$, $d = 5\ \mu m$ and $d/P = -0.3$; P = natural helical pitch of cholesterically doped LC-layer. The TN-LCD is operated in the first transmission minimum, $d = 6.0\ \mu m$, $\Delta n = 0.093$.

TABLE III

Some LCD applications.

Liquid Crystal Display (LCD)	APPLICATIONS
1) Conventional	Watches, Calculators
2) Medium Information Content	Typwriters, A6-size Matrices
3) High Information Content	
- 90° Twisted Nematic (TN) LCDs	A4-size Matrices
- Supertwist (STN) LCDs (mono and double layer)	Telephone, Telecom, Computer Terminals,
- Super Birefringence (SBE) LCDs	Graphics, Large Area Projection
- Optical Mode Interference (OMI) LCDs	
4) Outdoor	Automotive, Portable Instruments, Telecom
5) TFT-addressed Matrices	Direct View and Projection, Colour TV, Cockpits, Colour Graphics
6) Plastic LCDs	Traffic Signs, Electrically Tunable Windows
7) Guest-Host LCDs	Advertisement Boards
8) Ferroelectrics, Dual-Frequency Addressing	Fast Electro-Optical Shutters, Displays (High Info LCDs?)

gineers in the R & D departments as well as in the high quality production facilities of chemical and electronics industries.

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